Electrokinetic sonic amplitude (ESA) technique as a new tool to characterize zeta- potential of carbon fibers treated by plasma oxidation

Hamid Sarraf[1,2*], Ludmila Škarpová[1], Petr Louda[1]

[1] Faculty of Mechanical Engineering, Department of Materials, Technical University of Liberec, Halkova 6, 46117, Liberec 1, Czech Republic.
[2] Danish Polymer Centre, Risø National Laboratory, Frederiksborg vej 399, P.O. 49, DK-4000, Roskilde, Denmark
*Correspondence author. E-mail: sarraf_20002000@yahoo.com

ABSTRACT

The present work deals with the application of advanced electrokinetic sonic amplitude (ESA) technique as a new tool to characterize zeta- potential and isoelectric point of aqueous suspensions of polyacrylonitrile (PAN) based carbon fibers treated by plasma oxidation in the study. ESA technique proved that the oxygen plasma treatment resulted in a displacement of the isoelectric point of carbon fibers suspensions toward lower pHs, evidence of an increase in the surface acidity. ESA technique allows observation of changes taking place in the surface chemistry after modifications applied to industrially available unmodified carbon fibers. It is concluded that the measurement of the zeta-potential constitutes a useful technique to follow the evolution of the surface chemical characteristics of different types of carbon fibers.

INTRODUCTION

Oxygen plasma constitutes a novel and promising reactive medium for the surface chemical modification of different types of carbon materials, including graphites (1,2), meso-carbon microbeads (3-5), glassy carbons (6), carbon blacks (7), and carbon fibers (8). The oxygen plasma treatment of the latter type of material deserves particular interest as it can be used to improve the carbon fiber–matrix adhesion in composites by introducing oxygenated functionalities at the carbon fiber surfaces. This would lead, in turn, to composite materials with an improved inter-laminar shear strength.

Measurements of the electrokinetic or zeta potential have long been used to study the surface chemistry of different types of solids (9). This technique has been successfully applied to a range of carbon materials (10), with special emphasis placed on activated carbons. However, its application to characterize the surface chemical modifications accompanying the plasma treatment of carbon materials has been restricted to date to meso carbon microbeads (3-5). The application of electrokinetic measurements to carbon fiber surfaces is even more scarce. Grundke *et al.* (11) showed differences between the zeta potential–pH curves of untreated and oxidized carbon fibers, but the oxidation method employed was not specified.
In this work electrokinetic mobility (zeta potential-pH) measurements were carried out by using advanced electroacoustic ESA technique to compare the acid–base characteristics of carbon fibers oxidized to various extents in an oxygen plasma.

EXPERIMENTAL

The carbon fibers studied in this experiment were untreated and unsized PAN (polyacrylonitrile) - based type, with 12000 filaments per tow, manufactured by Tenax

Fibers GmbH Co. The plasma processing was carried out in a home-built inductively coupled cylindrical pulsed RF plasma reactor. A continuous flow of oxygen carrier gas was employed. The carbon fiber samples were treated in the chamber under a pressure of 4.0×10^{-1} mbar, and a current of 30 mA and 480V. The treatments in the oxygen atmosphere lasted 2 minutes.

ZETA POTENTIAL MEASUREMENTS - USING OF ESA TECHNIQUE

Electrokinetic potentials (zeta potentials) of parent (untreated) and oxidized carbon fiber samples in aqueous systems were determined with an advanced electrokinetic sonic amplitude (ESA) technique with a Model ESA-8000 from MATEC APPLIED SCIENCES in this study. This technique is able to determine simultaneously the electrokinetic (zeta potential, pH, electrophoretic mobility and isoelectric point) properties of different inorganic, polymers and ceramic materials in different concentrated suspensions using an SP-80 probe in a teflon vessel at a nominal frequency of 1 MHz.

The ESA instrument and its relative devices are shown in Figure 1. For each determination, 0.05g of sample was dispersed in 100 ml of 0.01 *M* KCl solution and the slurry magnetically stirred for at least 2h before the measurements were carried out. ESA measurements were recorded as the pH was titrated from pH 2 to pH 11.

To generate zeta potentials versus pH curves, and from them the isoelectric point (IEP), automatic titrations were performed using 0.1n HCl and KOH solutions followed by automatic magnetic stirring inside of the ESA teflon vessel.

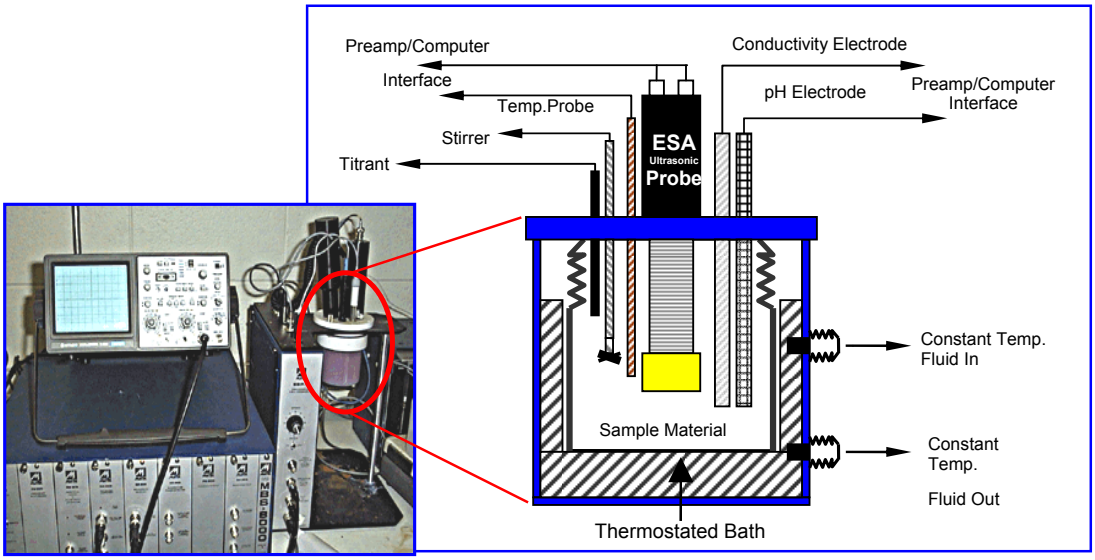


Figure 1. ESA-8000 system (Matec, Applied Science, USA) included by its SSP-1 sample Cell, as a new tool for zeta potential measurements of carbon fibers.

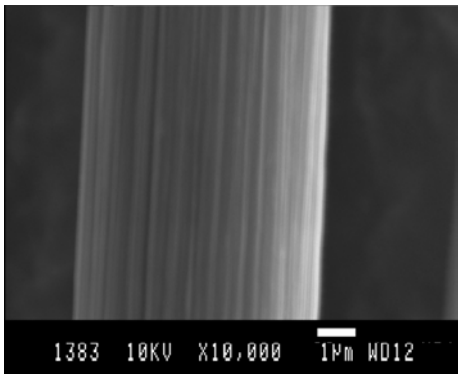
To insure pH stability and to determine the concentrations at which surface coverage is complete, pH was determined just before and just after each ESA measurements.

A temperature, pH, and conductivity probes detect the temperature, the pH, and the conductivity of the suspension during the measurement (see Figure 1).

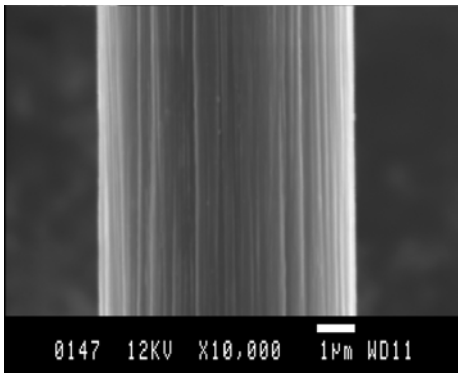
RESULTS AND DISCUSSION

Figure 2 (a,b) shows the SEM images of carbon fiber samples: (a) untrated and (b) treated by oxygen plasma for 2 minutes.

The diameter of carbon fibers ranged from 7 to 8 μm.



(a)



(b)

Figure 2. SEM image of carbon fiber samples: a) untreated and b) treated with oxygen plasma for 2 min.

The fiber treated with oxygen plasma for 2 minutes (Figure 2b) displayed superficial morphological changes and a striated pattern was observed along the fiber's axis. In this case, the striation depth was found slightly deeper than that observed in the untreated fiber.

Figure 3 shows the pH dependence of the zeta potential of the untreated and treated carbon fiber samples by plasma processing.

A negative value of the zeta potential over the entire pH range studied was obtained for plasma-treated sample, while the untreated sample presents an isoelectric point at a low pH value of (≈ 2.2).

This suggests that the carbon fiber sample treated by plasma for 2 min was oxidized as a consequence of plasma treatment, evidence of an increase in the surface acidity.

It was found that the effect of plasma treatment on the carbon fiber is being more noticeable the lower the structural ordering since oxygen readily adsorbs at carbon edge planes (12), comparing to the untreated carbon fiber.

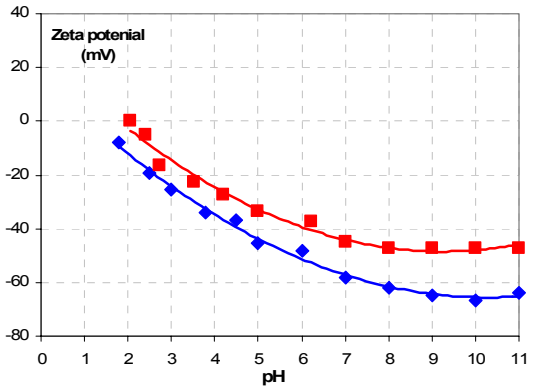


Figure 3. Zeta potential of untreated (■) and plasma treated (♦) carbon fiber samples as a function of the suspension pH in 10^{-2} *M* KCl.

The results from the electrokinetic (ESA) measurements through the pH-zeta potential dependency are in well agreement with the results obtained from surface analysis by SEM.

CONCLUSION

The surfaces of carbon fibers were physically treated using cold plasma in oxygen atmosphere, and the changes in the fiber surface chemistry were followed by zeta potential measurements using ESA technique. Morphological changes of the surfaces were monitored by scanning electron microscopy (SEM). The oxygen plasma treatment resulted in a displacement

of the isoelectric point of carbon fibers toward lower pHs, evidence of an increase in the surface acidity. The results obtained from SEM observation revealed a marked change in the topography of plasma-treated fibers, with well defined grooves and etching. Zeta potential measurements as well as SEM observations confirm changes at the fiber surface. Further, ESA technique and morphological (SEM) measurements complement each other. This allows observation of changes taking place in the surface chemistry after modifications applied to industrially available unmodified carbon fibers. It is concluded that the measurement of the electrokinetic properties constitutes a useful technique to follow the evolution of the surface chemical characteristics of different types of carbon fibers.

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REFERENCES

1. Donnet, J.-B., Parr, S. J., and Brendle, M., Carbon 30, 263 (1992).

2. Nakahara, M., and Sanada, Y., J. Mater. Sci. 29, 3193 (1994).

3. Sugiura, M., Esumi, K., Meguro, K., and Honda, H., Bull. Chem. Soc.Jpn. 58, 2638 (1985).

4. Esumi, K., Nishina, S., Sakurada, K., Meguro, K., and Honda, H., Carbon 25, 821 (1987).

5. Esumi, K., Sugiura, M., Mori, T., Meguro, K., and Honda, H., Colloids Surf. 19, 331 (1986).

6. Ohte, T., Katoh, M., Ohtani, S., and Kojima, A., Tanso 140, 268 (1989).

7. Donnet, J.-B., Wang, W.-D., Vidal, A., and Wang, M.-J., Carbon 32, 199 (1994).

8. Jones, C., and Sammann, E., Carbon 28, 509 (1990).

9. Jacobasch, H.-J., Prog. Org. Coat. 17, 115 (1989).

10. Lau, A. C., Furlong, D. N., Healy, T. W., and Grieser, F., Colloids Surf. 18, 93 (1986).

11. Grundke, K., Boerner, M.,& Jacobasch, H.-J., Colloids Surf. 58, 47 (1991).

12. Puri, B. R., *in* ‘‘Chemistry and Physics of Carbon’’ (P. L. Walker, Jr., Ed.), Vol. 6, p. 191. Marcel Dekker, New York, 1970.